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CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN ATOMS AT TEMPERATURES BELOW 100°K

by
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Preface

This report covers work performed from January 1, 1967 to June 30, 1967 under NASA grant NsG-337 (Supplement No. 1). A low graduate student enrollment during the past year has somewhat curtailed progress on this research, but we have recently added a number of new students such that there are now eleven predoctoral and postdoctoral students involved in the various activities of the Cryochemistry Laboratory. With several of these additional students being phased into the work of this grant, we anticipate reporting on progress in several other areas in our next Semi-Annual Report. Other than the principal investigator, people working on this program during this reporting period have included: two predoctoral students, Mr. R. J. Holt and Mr. P. H. Li, and one masters student, Mr. M. A. Bell. The work of each of these students, which has been fully supported by this grant, will also function in its entirety as fulfilling the research requirements for their respective degrees.

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I. INTRODUCTION

This research program is concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the Jovian planets. Each of these astronomical objects is very cold, and clearly insofar as chemistry plays a role in the behavior of these objects, this chemistry must be occurring at very low temperatures by terrestrial standards. This objective rather quickly resolves itself into studies of low molecular weight compounds of the four reactive elements of maximum cosmic abundance, namely hydrogen, carbon, nitrogen and oxygen.

The approach here is not one of free radical stabilization or of an attempt to isolate labile species in an inert matrix at very low temperatures. All evidence to date suggests that the activation energy for the reaction of low molecular weight free radicals is zero (or close to it), and hence it will be possible to prepare these species in "stable" forms only by diffusional inhibition techniques such as inert matrix isolation. The concentrations of such labile species that have been prepared are then limited to usually a few tenths of a per cent, and hence the importance of matrix isolated free radicals in cosmic chemistry would seem to be minimal. The matrix technique, particularly when combined with ir or epr, does, of course, provide a powerful means to study the physical and chemical properties of free radicals. By contrast, low molecular weight labile species which have singlet electronic ground states, i.e., species that are highly reactive but are not free radicals, are in an altogether different category. Typical species of this class are substances like cyclobutadiene, cyclopropanone, oxirene, diimide, ammonium ozonide, benzyne, tetrahedran, and many others. This serves to indicate the kind of molecule that is being discussed. One would expect these species to exhibit an activation energy for reaction, but we would also expect this energy to be unusually small. If an activation energy exists, then substances such as these may be preparable as stable cryochemical reagents and a true chemistry at very low temperatures may be developed. Since the activation energies involved in these systems is small, it will usually be necessary to maintain the compounds below some critical temperature if they are to be manipulated as stable, pure reagents. This means that manipulative techniques must be developed for use with unstable substances at cryogenic temperatures. Ideally, one would like to transpose all of the common or usual operations of bench scale chemistry to the point of convenient use at cryogenic temperatures. The most important operation in any chemical investigation is analysis. In past reports on this grant and its precursor, NsG-337, the development of a cryogenically cooled reactor-inlet system attachment to a time-of-flight mass spectrometer has been described in detail. The cryogenic mass spectrometer continues to be the key analytical tool in the approach to low temperature chemistry that is being pursued in this laboratory.

II. EQUIPMENT

We continue to put reliance upon the Bendix time-of-flight mass spectrometer as our primary analytical tool for the investigation of very low temperature chemical systems. Three of these instruments are now operative in the Cryochemistry Laboratory. A significantly redesigned cryogenic reactor-inlet system is now under construction but at no cost to the grant. The new system draws heavily upon our experience with existing reactor-inlet arrangements, but it promises to be a rather more versatile system. Its design and operation will be described in a forthcoming paper, preprints of which will be forwarded to NASA as soon as they are available.

The NASA owned Model 14-107 Bendix mass spectrometer is not sufficiently instrumented to allow ionization efficiency measurements to be performed. Yet such measurements are a necessary part of our identification procedures that have been rather highly developed for use with unstable chemical systems at very low temperatures. In addition, the ionization efficiency measurements permit one to develop the molecular energetics of these cryochemicals. Rather than merely duplicating the existing ionization efficiency instrumentation on one of the other spectrometers, it has seemed advisable to reevaluate the equipment and technique with a view toward their possible improvement. Several points are being explored:

1. The fact that the Bendix spectrometer is pulsed (10 kc) provides a ready-made, ideal possible application for phase sensitive detection using a lock-in amplifier. This would greatly increase the signal to noise ratio and hence make possible (1) energetic measurements at much lower temperatures, and (2) more accurate energetic measurement at all temperatures. We insist upon a minimum precision of ± 0.1 e.v. in these data.

2. It is important to be able to perform an energetic measurement rapidly during the course of an experiment. Present techniques, both in this laboratory and elsewhere, require that the raw data be taken in a 1/2 to 1 hour operation followed by manipulation of these data requiring 1 to 2 additional hours before a final appearance potential is obtained. It appears that a plot of the ionization efficiency data using an X-Y plotter could reduce this entire operation to a required time of 1/4 to 1/2 hour.

3. It is well known that the effective life of the dynode and field strips of the Bendix magnetic electron multiplier can be greatly lengthened if electrons corresponding to undesired or uninteresting ions are prevented from entering the multiplier. This problem has been extensively investigated at Argonne National Laboratory, and a rather simple circuitry has been developed which permits only the ions of interest to enter the multiplier. Complete descriptions of the apparatus have been kindly furnished by ANL. The linearity of the multiplier may also be enhanced by use of the Argonne filter apparatus, and the linearity is particularly important in ionization efficiency measurements.

III. RESEARCH

Some of the most interesting problems in astrochemistry, particularly as regards cometary phenomena, are concerned with the types of compounds and reactions that occur under environmental conditions that are very extreme by terrestrial standards. Spectral observations prove the presence of CN, C_3, NH_2, C_2, OH, NH, and CH in comet heads. The parent compounds from which these species originate may be only conjectured, but in view of the very low temperature of the comet it seems clear that unusual and highly reactive parent species may well be present. Consequently, an important phase of this NASA program is the synthesis, reactivity, structure and energetics of principally C - H and N - H compounds that are of low molecular weight, are highly reactive, and which may exist only at very low temperatures. However, as long as these species are kept cold, they may be distilled, purified, reacted, etc. just as would any normal reagent at more ordinary temperatures.

Several studies in this low temperature, preparative chemistry are being pursued, and the progress on each is categorized below with respect to the particular sought-for product molecule.

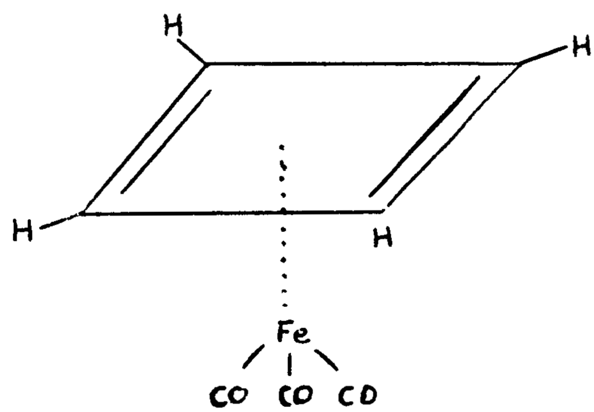
A. CYCLOBUTADIENE

Cyclobutadiene is a cyclic and highly reactive dimer of acetylene. It has never been isolated, although it has been frequently discussed by organic chemists for many years. Acetylene is a postulated cometary constituent, and if this be true, then it seems entirely reasonable that the dimer, C_4H_4, might also be present in icy cometary nuclei. Cyclobutadiene seems sure to exhibit interesting chemistry, the relevancy of which to cometary phenomena could be significant. Thus, it has seemed reasonable to explore (1) the synthesis, (2) proof of existence, (3) isolation, (4) energetics and (5) the most simple reactivity of cyclobutadiene using the techniques of cryochemistry. It has further turned out, perhaps fortuitously, but nonetheless interestingly, that the only promising route to cyclobutadiene involves a newly synthesized parent substance in which the hydrocarbon is complexed with iron tricarbonyl. Now iron is also apparent in comet spectra at approximately 0.01 AU, and it is conceivable that this iron is present in the icy cometary nuclei as a complex with some highly reactive, unstable hydrocarbon such as cyclobutadiene. Nickel also forms similar highly reactive and volatile hydrocarbon and carbonyl complexes. It appears then, that both the parent molecule as well as the free hydrocarbon ligand could be of interest in cometary chemistry considerations. Molecules of cyclobutadiene with iron as well as the other transition metals may exist at low temperatures in configurations analogous to dibenzyl iron or ferrocene.

In 1956, Longuet-Higgins and Orgel[1] predicted the stability of complexes of cyclobutadiene with certain transition metal carbonyls. In 1965, Pettit and

[1] H. C. Longuet-Higgins and L. E. Orgel, J. Chem. Soc., 1969 (1956).

co-workers at the University of Texas reported the first stable cyclobutadiene complex, cyclobutadieneiron-tricarbonyl, CIT.[2] The geometry of this complex is still unknown, but the geometry of the four proton system has recently been determined from nmr studies.[3] It is clear that the proton geometry is, within experimental error, square, i.e., the ratio of adjacent sides of the "rectangle" were found to be 0.9977 ± 0.0045. This deduction was based on the observation of the nematic pmr spectrum of CIT at 76° which appeared as a symmetric eight-line multiplet. As usual TMS was employed as an internal reference. Thus, this observation of the square configuration of the four protons, together with the earlier indirect indication of a square configuration of the carbon skeleton[4], suggest that the structure of CIT should best be visualized as,



where the carbons and the protons are co-planar.

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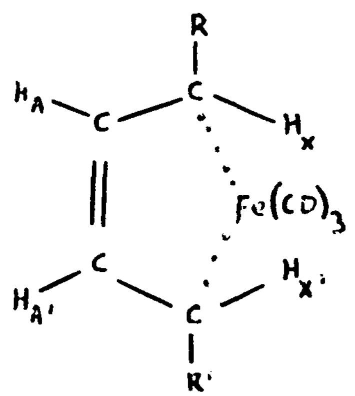
[2] G. F. Emerson, L. Watts and R. Pettit, J. Am. Chem. Soc., 87, 131 (1965).

[3] C. S. Yannoni, G. P. Ceasar and B. P. Dailey, J. Am. Chem. Soc., 89, 2833 (1967).

[4] J. D. Fitzpatrick, L. Watts, G. F. Emerson and R. Pettit, J. Am. Chem. Soc., 87, 3254 (1965).

It is perhaps interesting to compare the above situation with that of the addition of the iron atom across the similar 1,4 diene system to yield complexes like,



Here, the four carbon atoms that were the 1,4 diene before complex formation are coplanar. But Fe is below, H_x and H_x' are above and H_A and H_A' are somewhat below the plane of the carbon skeleton. These observations are also deduced from nmr data.[5]

In earlier reports we have reported the successful duplication of the Texas synthesis of CIT first reported in 1965. We have compared the boiling

[5] H. S. Gutowsky and J. Jonas, Inorg. Chem., 4, 430 (1965).

point, infrared spectra and pale yellow color of the CIT that we synthesized with those properties reported by Petitt[2,6], and it was evident that we have obtained the same compound. We also have, more recently, determined the low resolution nmr spectrum of CIT which consists of a single sharp absorption at τ6.09 relative to TMS which also confirms Pettit's result[2].

The ionization potential of CIT was measured as 8.5 ± 0.1 e. v. This ionization potential was determined by the semi-log and linear intercept methods with the energy scale calibrated immediately before and after each energy measurement using argon. It is interesting to compare this result with the ionization potential of $C_6H_8Fe(CO)_3$ of 8.0 ± 0.4 e.v. which was determined by Winters[7]. This suggests that in such complexes, the electron is removed from an iron orbital in the ionization process. Further confirmation of this idea is apparent in the similarity of the ionization potentials of a number of hydrocarbon metal carbonyls as well as metal carbonyls themselves. Table I contains a summary of such data.

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6 L. Watts, "Cyclobutadieneirontricarbonyl," Ph.D. Thesis, Univ. of Texas, 1966.

7 R. E. Winters, Ph.D. Thesis, Kansas State University, 1965.

TABLE I

IONIZATION POTENTIALS OF CARBONYLS

Carbonyl	Ionization Potentials: Carbonyl	Ionization Potentials: Metal	Reference
$Co_2(CO)_8$	8.12	7.81	8
$Mn_2(CO)_{10}$	8.55	7.43	8,9
$Re_2(CO)_{10}$	8.27	7.87	9
$ReMn(CO)_{10}$	8.15	7.43, 7.87	9
$C_6H_8Fe(CO)_3$	8.0	7.83	7,10
$C_5H_5Mo(CO)_2(NO)$	8.1	7.35	10
$Fe(CO)_5$	8.53	7.83	11 a
$Mo(CO)_6$	8.23	7.35	11 b

Since the ionization potential of CO is about 14 e.v., it seems clear that ionization involves the removal of a valence electron from the metal atom.

CIT was readily sublimed into the source, and there was no evidence of its thermal decomposition. The isotopic abundancies were as expected and in keeping with accepted values.

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[8] R. E. Winters and R. W. Kiser, J. Phys. Chem., 69, 1618 (1965).

[9] H. J. Svec and G. A. Junk, J. Am. Chem. Soc., 89, 2836 (1967).

[10] R. E. Winters and R. W. Kiser, J. Phys. Chem., 69, 3198 (1965).

[11a] R. E. Winters and R. W. Kiser, Inorg. Chem. 3, 699 (1964); [11b] Inorg. Chem. 4, 157 (1965).

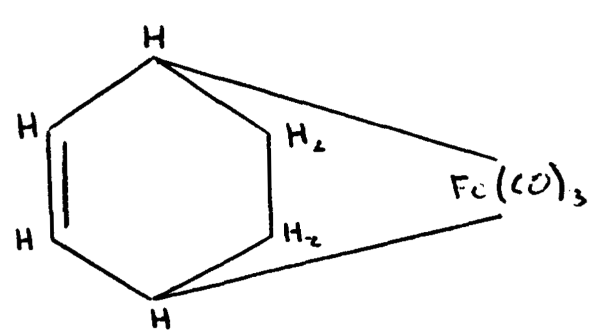
Some comparisons between the spectrum of CIT and other hydrocarbon metal carbonyls and related compounds is of interest.

TABLE II

TRANSITION METAL CARBONYLS STUDIED BY MASS SPECTROMETRIC TECHNIQUES

	Compound	Reference
I	$C_5H_5Mo(CO)_2NO$	10
II	$C_6H_8Fe(CO)_3$	10
III	$C_6F_8Fe(CO)_3$	12
IV	$C_4H_4Fe(CO)_3$	This work

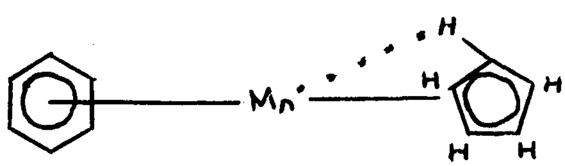
The mass spectra of each of the compounds in Table II show ions formed by the successive, removal of the carbonyl (or nitrosyl) entity. $FeCO^+$ and $Fe(CO)_2^+$ ions are present in II and IV, but II loses H_2 to form $C_6H_6Fe^+$ rather than $C_6H_8Fe^+$, in fact, this latter ion is completely absent from the spectrum of II. The $C_6H_6Fe^+$ ion is present to 57.8% of the most prevalent ion, and it is the second most dominant ion in the spectrum of II, while the corresponding $C_4H_4Fe^+$ is the most prevalent ion in the spectrum of IV. This perferential loss of H_2 in II may be pictured in terms of a postulated structure,



[12] H. H. Hoehn, L. Pratt, K. F. Watterson and G. Wilkinson, J. Chem. Soc., 2738 (1961).

whose resemblance to that of non-cyclic iron-dienes is apparent. It seems reasonable that such a structure would be less strained and more stable by the formation of the symmetric diene structure. A second point of interest is the low abundance of $Fe(CO)_x^+$ ions in the spectrum of both II and IV, whereas these ions are the most abundant in the spectrum of III. This suggests that the hydrocarbon-iron bond in II and IV is greater than that in the corresponding perfluoro derivative such as III.

A third point of interest is the presence of metal-hydrocarbon ions containing smaller hydrocarbon fragments than the original ligand. For example, $C_3H_3Mo^+$ is 95% of the dominant ion, $C_5H_5Mo^+$, in I, and $C_2H_2Fe^+$ is 80% of the dominant ion, $C_4H_4Fe^+$, in the mass spectrum of IV. The presence of such fragmented hydrocarbon-metal ions is also noted in ferrocene Cp_2Fe [13], BzCpMn[14] and Bz_2Cr[14]. (Here Cp = cyclopentadienyl and Bz = benzene). Bimolecular reactions in the source leading to the fragmented hydrocarbon are unlikely due to the low source pressure, for if, e.g., $MnBz^+$ existed long enough to undergo such a bimolecular reaction, it would have assuredly appeared in the mass spectrum; but it did not. This has led to the postulate of a concerted decomposition mechanism,[14]



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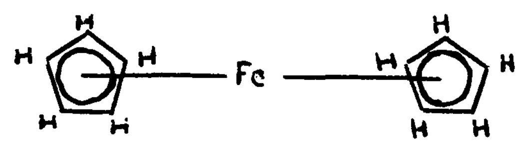
[13] F. W. McLafferty, Anal, Chem., 28, 306 (1956).

[14] R. G Denning and R. A. D. Wentworth, J. Am. Chem. Soc., 88, 4619 (1966).

in which the hydrogen atom attaches itself to the metal atom as the C_5H_4 fragment is leaving. Similar ion decomposition mechanisms have been envoked in discussing the fragmentation pattern of substituted ferrocenes,[15] but ferrocene itself,



shows no evidence of a similar mechanism being operative, i.e., $C_5H_5 - FeH^+$ does not appear in its spectrum.

Production of Free C_4H_4 from CIT

Studies of the pyrolysis of CIT have been conducted in a coaxial furnace inlet system in which the furnace exhaust is only 1/8 in. from the ionizing electron beam of the mass spectrometer.[16] Both 1/8 and 3/16 in. O.D. pyrex glass furnaces have been used. In both furnaces, the maximum intensity of m/e 52 (i.e., free cyclobutadiene) was observed at 380°. The dominant peaks of the pyrolysis products using 70 e.v. electrons and their assignments are summarized in Table III.

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[15] A. Mandelbaum and M. Cais, Tetrahedron Letters, 3847 (1964).

[16] H. A. McGee, Jr., Final Report on NASA grant NsG-337, July, 1966.

TABLE III

MASS SPECTRUM OF THE PRODUCTS FROM THE PYROLYSIS OF CYCLOBUTADIENEIRONTRICARBONYL AT 380°C

m/e	Assignment
104	$C_8H_8^+$
78	$C_6H_6^+$
56	Fe^+
52	$C_4H_4^+$
51	$C_4H_3^+$
50	$C_4H_2^+$
44	$C_3H_8^+$
39	$C_3H_3^+$
28	CO^+
27	$C_2H_3^+$
26	$C_2H_2^+$
16	O^+
12	C^+
2	H_2^+

Since the mass spectrum of cyclooctatetraene (C_8H_8) does not have a peak at m/e 52, but benzene (C_6H_6) does have such a peak, one might well question whether the 52 peak is a fragment of benzene, free cyclobutadiene or free vinyl acetylene ($H_2C = CH - C \equiv CH$). The intensity of m/e 52 from C_6H_6 at 70 e.v. is only 20% of the intensity of $C_6H_6^+$. In our spectra the intensity of m/e 52 is 40% of m/e 78 and hence the remainder must be due either to free cyclobutadiene or to vinyl acetylene. A calibration experiment with vinyl acetylene will resolve this uncertainty, as will a measurement of the appearance potential of m/e 52. Both of these tasks are now underway.

From the photolysis of CIT, Gunning et al.[17], in very recent work, (May 1967) have tentatively observed free cyclobutadiene. This constitutes the nearest to unequivocal observation of cyclobutadiene that has yet been reported. Dominant peaks of the photolysis products in the mass spectrometer were m/e = 26 ($C_2H_2^+$), 52 ($C_4H_4^+$), 78 ($C_6H_6^+$), 104 ($C_8H_8^+$), 140 ($Fe(CO)_3^+$) and Fe^+, CO^+. We failed to observe m/e 140 ($Fe(CO)_3^+$) which is evidently due to the decomposition of $Fe(CO)_3$ at 380°C. Supporting evidence that the C_4H_4 species contained an unbranched carbon chain have been shown by Gunning[17] in the formation of furan in an experiment in which CIT was photolyzed in the presence of oxygen.

The appearance potential of $C_4H_4^+$ from C_6H_6 is 15.6 ~ 15.9 e.v.,[18] and the ionization potential of vinyl acetylene is 9.9 ± 0.09 e.v.[18]. The appearance potential of $C_4H_4^+$ in our mass spectrum has not been measured accurately. But this is underway, and clearly the difference in the value of $I(C_4H_4^+)$ from $A(C_4H_4^+)$ from C_6H_6 and $I(C_4H_4^+)$ from vinyl acetylene, will further support the hypothesis that free cyclobutadiene is obtained from our pyrolysis experiments with CIT. The measurement of $A(C_2H_2^+)$ from CIT will also permit one to deduce the heat of formation of this molecule.

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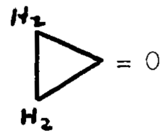
[17] H. E. Gunning, et al., <u>Chem</u>. <u>Comm</u>., No. 10, 497 (1967).

[18] F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Academic Press, New York, N. Y., 1957.

The reaction of CIT with ceric ammonium nitrate in ether solution has also been carried out. This is the same reaction that was used by Pettit in his original studies that led to the first indirect data suggesting that free cyclobutadiene many be producible.[4] CIT in ether was added to aqueous ceric ammonium nitrate solution at 0°C. The gas evolved was passed through a tube kept at 0° and was quenched at -197° in our cryogenic inlet system attached to the mass spectrometer.[16] Mass spectra were observed during a slow warm-up period. We failed to detect m/e 52 but m/e 104 appeared at -100°. Experimental difficulties caused the temperature of the inlet system to increase to -160° before the mass spectra could be observed. Hence, if free cyclobutadiene was evolved, it very likely was pumped away. Whether this m/e 104 is the cyclobutadiene dimer or cyclooctatetraene also requires further investigation.

B. CYCLOPROPANONE

Recent evidence obtained in this laboratory strongly suggests that we have synthesized cyclopropanone,



as a free, stable cryochemical which will remain unreactive up to temperatures approaching that of dry ice (-78°). In view of the presence of the carbonyl carbon, one would expect the three-membered ring of cyclopropanone to be highly strained. Due to its theoretical importance as a proposed organic reaction intermediate, the synthesis of cyclopropanone has been the subject of much research activity which has however proved unsuccessful until the past year.[19,20]

The reaction of diazomethane with ketene affords a direct approach to the synthesis of cyclopropanone:

$$\underset{(42)}{CH_2N_2} + \underset{(42)}{CH_2CO} \rightarrow \underset{(56)}{\underline{cy}\text{ - }CH_2CH_2CO} + \underset{(28)}{N_2} \tag{1}$$

Room temperature attempts of this synthesis have always yielded the butanone which was viewed as resulting from further reaction of diazomethane with cyclopropanone:

$$\underset{(42)}{CH_2N_2} + \underset{(56)}{\underline{cy}\text{ - }CH_2CH_2CO} \rightarrow \underset{(70)}{\underline{cy}\text{ - }CH_2CH_2CH_2CO} + \underset{(28)}{N_2} \tag{2}$$

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[19] N. J. Turro and W. B. Hammond, J. Am. Chem. Soc. 88, 3672 (1966).

[20] S. E. Schaafsma, H. Steinberg, Th. J. De Boer, Rec. Trav. Chim. 85, 1170 (1966).

Our interest has been to determine whether the techniques of cryochemistry permit the synthesis and isolation of cyclopropanone by the above reaction and the observation of its stability, mass spectrum, energetics and reactivity.

As discussed in an earlier report,[21] explosive diazomethane and toxic ketene are prepared, purified and finally analyzed using the T.O.F. mass spectrometer. The mass spectrometric data confirm the presence of the desired reagents and the absence of m/e = 56 and m/e = 70. The reaction of diazomethane and ketene was carried out in a cooled, evacuated trap by arranging, at liquid nitrogen temperature (77°K), a ring of diazomethane above a ring of ketene (in great excess) and then plunging the trap into a dewar held at -150° whereupon the solid yellow diazomethane became a viscous liquid which slowly ran down into and reacted with the now also liquid ketene producing a white solid and a volatile gas. The solid product (which should have a higher reaction energy of activation than the gas or liquid) combined with the low temperatures should deter any further reaction of the initial products.

The product gas proved to be uncondensable at 77°K and exhibited a two line mass spectrum at m/e = 28 and m/e = 14 in proportions nearly that of nitrogen indicating that the product gas was nitrogen and that reactions (1) and/or (2) were probably occurring. After the excess reactants (which was proved to consist entirely of ketene) was removed by warming and pumping on the reactor, the solid product was transferred to the cryogenic inlet system,[16] where it was warmed until it exerted a sufficiently high vapor pressure ($10^{-5} \sim 10^{-3}$ torr) to be analyzed in the mass spectrometer. Product peaks corresponding to m/e = 56 and m/e = 70 were observed and studied at -90° and -75° respectively.

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[21] J. A. Knight, Jr. Second Semi-Annual Report on Grant NsG-337 (Supplement No. 1) January 1967.

The volatilities of the two species allowed them to be separated sufficiently to obtain their mass spectra (see Figures 1 and 2). The vapor pressure, mass spectra, and energetic values of the heavier sample (maximum m/e 70) of our product were very similar to the same data obtained in this laboratory from a sample of pure cyclobutanone (purchased from K & K Laboratories, Plainview, New York, #3906, and used without further purification). In interpreting the experimental traces shown in Figures 2 and 3, the following facts were taken into consideration: a large air leak produced peaks at m/e = 32, 16, 28, 14 and 29; background water causes peaks at m/e = 18 and 17; the calibrating gas argon has peaks at m/e = 40 and 20; impurity acetone and product cyclopropanone exhibit peaks at 58, 43 and 15; and 56, 42, 41, 28, 27, and 26 respectively. A comparison of the heavier product (maximum m/e = 70) and pure cyclobutanone is made in Table IV. The mass spectra of the lighter sample (maximum m/e = 56) exhibited the same major ions as those reported by Schaafsma[20] for cyclopropanone. (See Table IV).

TABLE IV

MASS SPECTRA OF CYCLIC KETONES

	Percent of Peak of Maximum Intensity															
Source	m/e 70	56	42	41	40	39	38	37	36	29	28	27	26	25	24	14
Cyclobutanone[22]	30	0	100	9	2	9				7	8	6				6
Cyclobutanone (this work)	22	0	100	12	?	14	5	4	2	?	?	12	8			?
Product m/e = 70 (this work)	20	0	100	14	?	16	5	5	2	?	?	12	8			?
Cyclopropanone[20]		18	14								100	38	38			
Product m/e = 56 (this work)		15	15	5	?	4	4	4	3	?	100	35	34	4	1	?

[22] H. J. Hofman, Tetrahedron Letters No. 34, 2329 (1964).

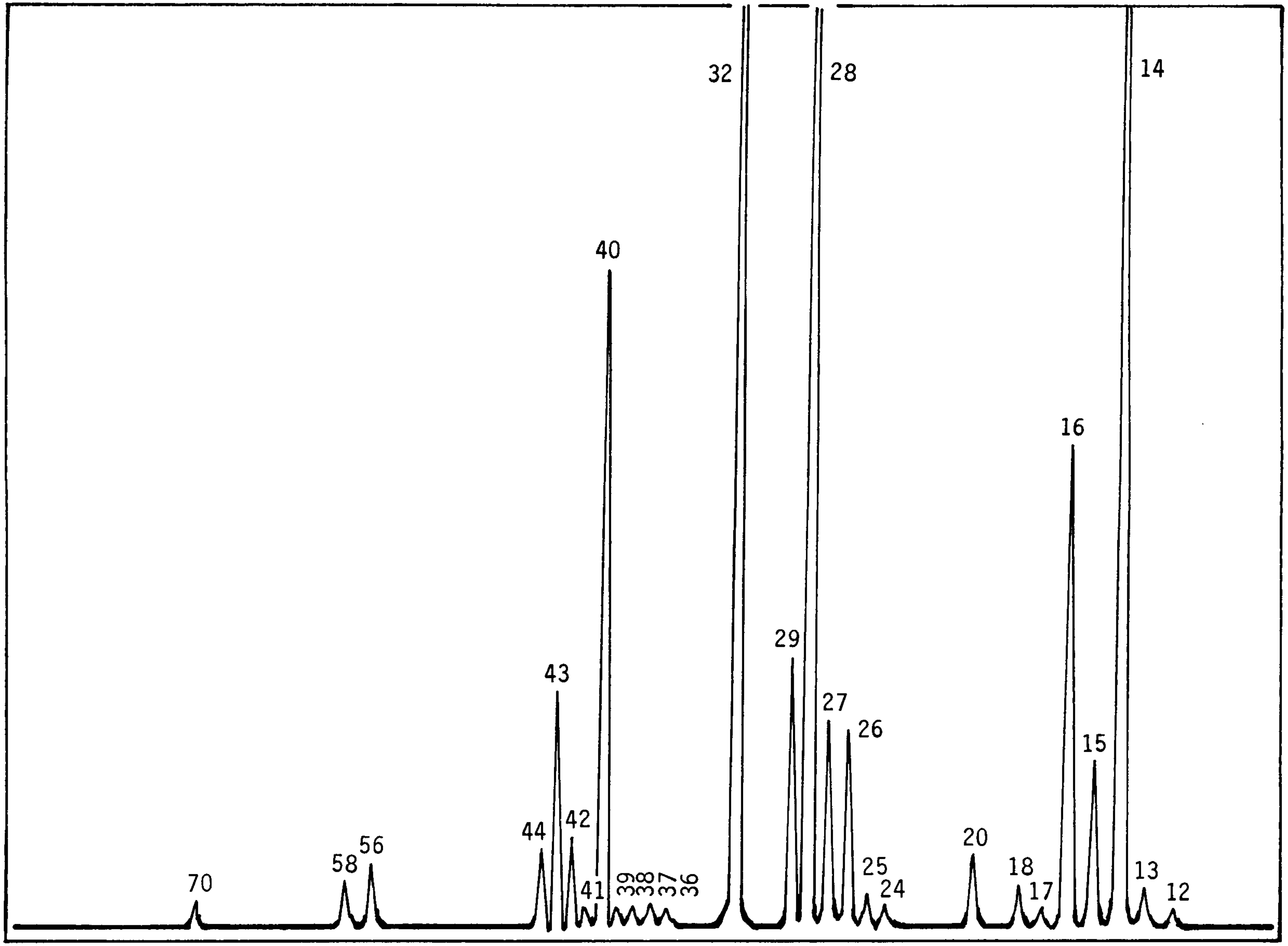


Figure 1. Mass spectrum of light product (maximum m/e 56) from ketene-diazomethane reaction. Spectrum obtained with cryogenic inlet system at -90° and using 70 e.v. electrons.

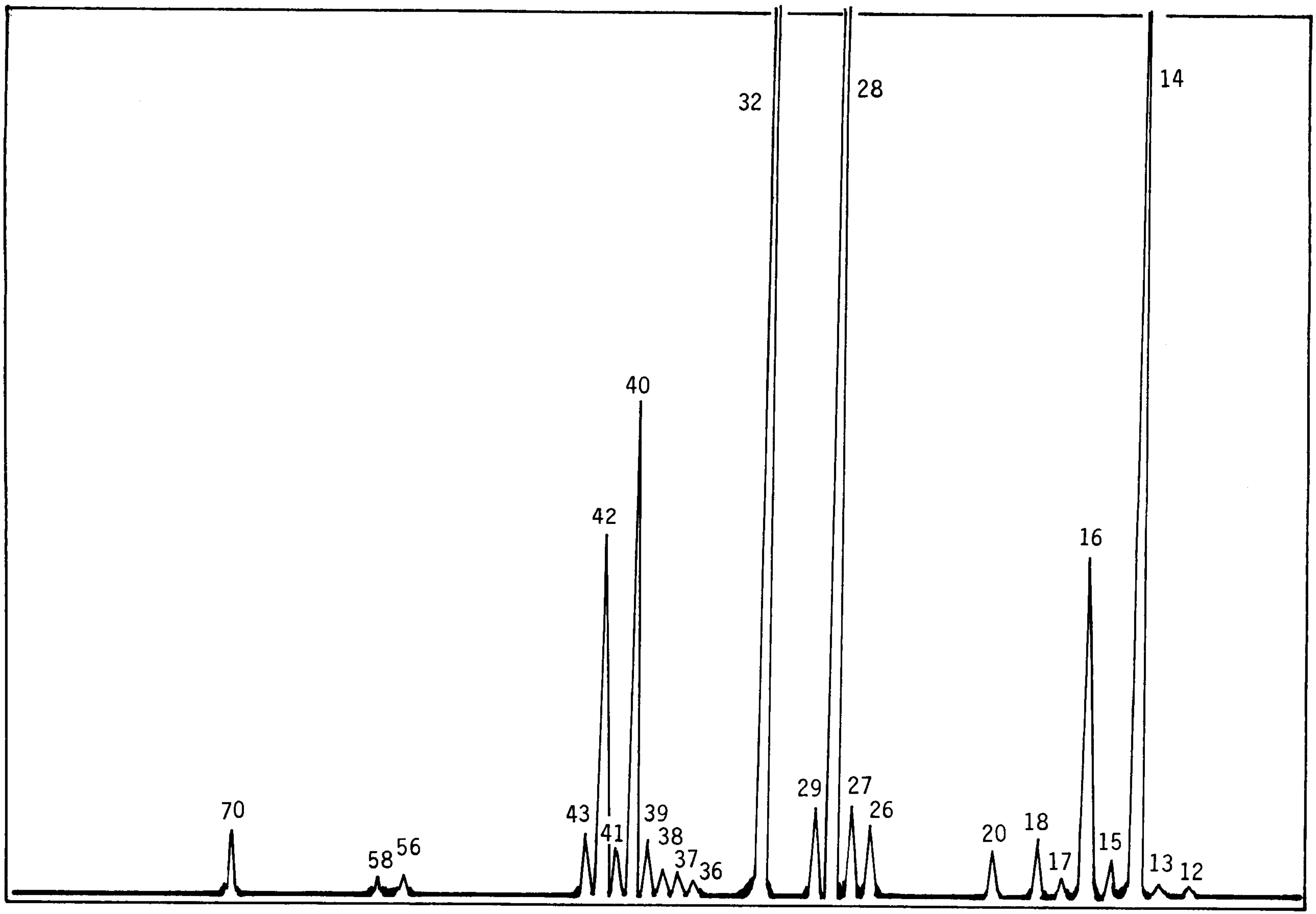


Figure 2. Mass spectrum of heavy product (maximum m/e 70) from ketene-diazomethane reaction. Spectrum obtained with cryogenic inlet system at -75° and using 70 e.v. electrons.

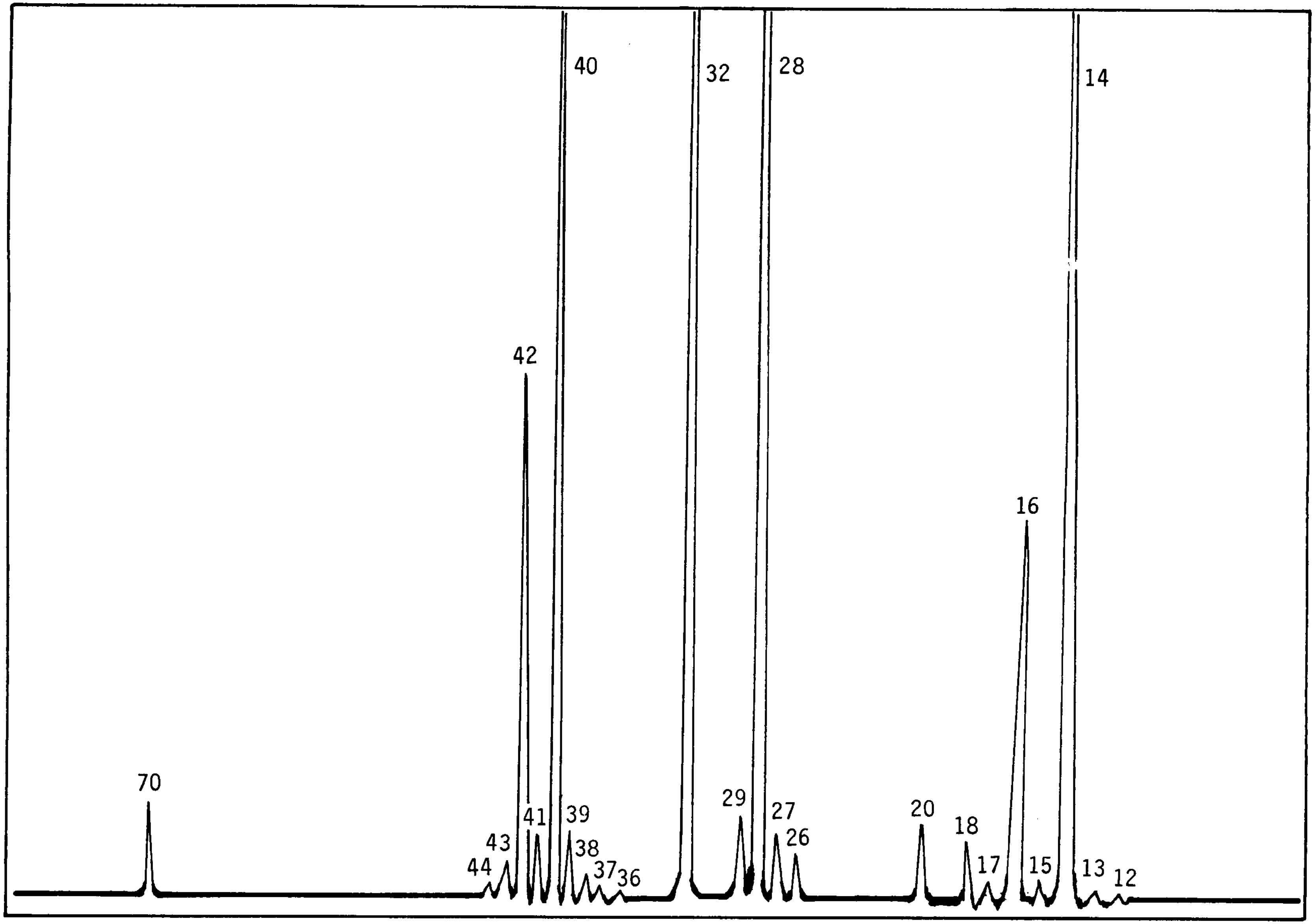


Figure 3. Mass spectrum of cyclobutanone with cryogenic inlet system at -75° and using 70 e.v. electrons.

Although m/e = 28 could not be determined accurately (air leak), the relative intensities of m/e = 56, 42, 27 and 26 agree well with the data of Schaafsma. This leads one to conclude that our heavy sample corresponds to cyclobutanone and resulted from further reaction of the lighter product, cyclopropanone. Cyclopropanone and cyclobutanone yield the same ions upon electron bombardment revealing their similar structure.

We have studied the effect of temperature on the stability of the lighter and heavy species by soaking isolated samples of each at various temperatures, following this by a quench and subsequent warmup and analysis. Cyclopropanone appears to be stable indefinitely at temperatures from -196° to -145° probably because it is a solid with a negligible vapor pressure. Some, if not all, of the cyclopropanone retained its identity after a one hour, -90° soaking. Although a one hour room temperature soaking revealed that cyclopropanone had been destroyed, no volatile reaction products were observed. A non-volatile, white, waxy substance soluble in acetone remained in the soaking trap which is in agreement with evidence[19,20] that cyclopropanone reacts with itself to form a polymer. In view of these results, it is evident that cyclopropanone does not decompose, that, in fact, its ring may remain intact, but which, as a gas, is very reactive. Monel metal or glass surfaces did not effect the above results. Cyclobutanone retained its identity throughout all stability experiments.

Some preliminary ionization efficiency data are reported in Table V, and an example of the type of data obtained is shown in Figure 4 wherein the ionization potential of cyclopropanone appears to be 0.4 e. v. lower than that of cyclobutanone.

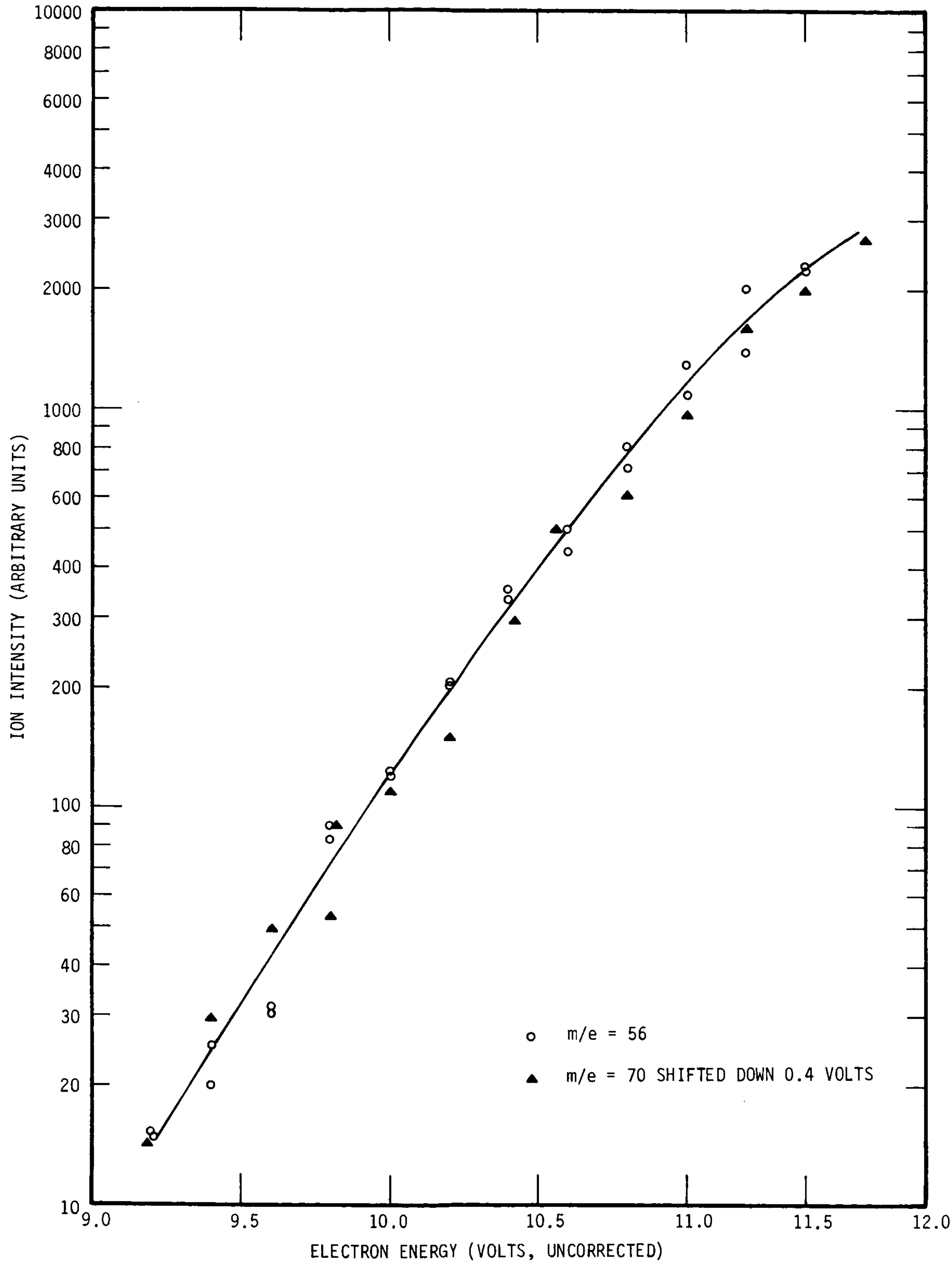


Figure 4. Semi-log plot of ionization efficiency data for ions m/e 56 and m/e 70. The data for m/e 70 have been shifted 0.4 e.v. indicating that the ionization energy of cyclopropanone is 0.4 e.v. less than the ionization energy of cyclobutanone.

TABLE V

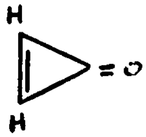
IONIZATION AND APPEARANCE POTENTIALS FROM CRYOCHEMICAL SYNTHESIS EXPERIMENTS

Parent Compound	Fragment Ion Appearance Potentials (e.v.) m/e 70	56	42	28
Cyclobutanone	9.7		11.0	
Product m/e = 70	9.6		11.2	10.2
Product m/e = 56		9.3	10.5	9.9

The incomplete separability by volatility of m/e = 56 and m/e = 70 proved troublesome in obtaining energetic data because even low ion intensities of the same m/e may be significant. In addition, both cyclopropanone and cyclobutanone exhibit observable peaks at m/e = 40, 32, and 28 which interfere with three commonly used calibrating gases (argon, oxygen, and nitrogen). These experimental difficulties are being resolved. The energetics of cyclopropanone and cyclobutanone should prove to be challenging due to the added feature of the simultaneous cleavage of two bonds during fragmentation of the ring structure.

C. CYCLOPROPENONE

Cyclopropenone,



is a highly strained, small ring system that appears to possess considerable conjugative stabilization. Studies with the substituted molecule date from 1959, and compelling, but not absolutely conclusive, evidence for the synthesis of the parent ketone has appeared within the past few weeks.[23] The synthesis yields the ketone in aqueous solution, but attempts to isolate the substance, whether by removal of the solvent by distillation, or by vapor phase chromatography under a variety of conditions have so far failed. Cyclopropenone is lost by polymerization just as is true of the hydrogenated analog, cyclopropanone. However, the olefin appears to be more stable than the saturated compound.

Both of these ketones are interesting cryochemical systems. The cyclopropene is particularly interesting in view of the failure of standard techniques in attempts to isolate the substance. The cryochemical equipment and procedures that have been developed in this laboratory will be applied to the isolation, energetics, and reactivity questions that represent fundamental gaps in our understanding of this brand-new and exciting molecule. This comment and stated objective is in no way to dimish the creativity and originality of Dr. Breslow's work, but it is rather to suggest that the techniques of cryochemistry may well be the only way to effectively study this most interesting molecule.

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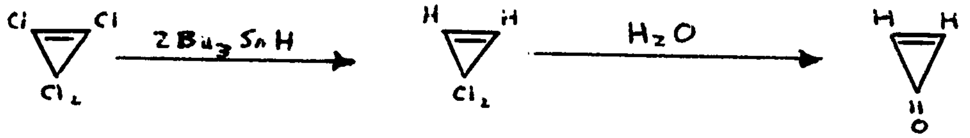
[23] R. Breslow and G. Ryan, _J. Am. Chem. Soc._ _88_, 3073 (1967).

It has seemed appropriate to briefly recapitulate the synthesis of cyclopropenone at this point.

Reaction of tetachlorocyclopropene with two equivalents of tri-n-butyltin hydride at room temperature in paraffin oil produced a volatile mixture of mono -,di-, and tri-chlorocyclopropenes, one of which is 3,3-dichlorocyclopropene. This mixture of chloronated isomers may, upon distillation, be separated and the desired 3,3 isomer may be absorbed in CCl_4. Upon hydrolysis of this solution with cold water, the aqueous phase yields a single nmr signal at $\delta = 9.0$ (relative to tetramethylsilane) which may be assigned to the protons of cyclopropenone. This sequence of reactions may be represented schematically as follows:



The required tetrachlorocyclopropene may be easily synthesized from readily available materials in the following way:

A.[24] Trichloroethylene (2500 ml) and trichlorosodium acetate (1600 gm) may be mixed and stirred under reflux until dry. Then 750 ml of dry 1,2-dimethoxyethane are added to the flask whereon CO_2 evolution is immediate and the solution darkens. Reflux, accompanied by CO_2 evolution and darkening, continued at 80° for 2.5 days. Approximately 500 ml of a dark brown oil was then obtained from the crude reactant solution. The oil was distilled and the fraction boiling at 75° at 20 torr was a colorless, minty smelling oil, which was pure pentachlorocyclopropane. The above quantities yielded 390 gr. of product, or about 22% yield based on tri-chlorosodium acetate.

[24] S. W. Tobey and R. West, J. Am. Chem. Soc. 88, 2478 (1966).

B.[25] The pentachlorocyclopropane now needs only to be dehydrohalogenated (-HCl) to yield the desired tetrachlorocyclopropene. The cyclopropane derivative (50 gm) was added to 0.6 moles of KOH in 40 ml of water, and the reaction mixture was kept at 85-95° for 30 min. Upon cooling and acidification with HCl, the emulsion broke and about 25 ml of an oily layer was separated off. Simple distillation of this oil under nitrogen at 129-133° provided about 33 gms of clear, colorless tetrachlorocyclopropene.

The above syntheses, A and B, have been taken directly from references (24) and (25). The amounts of reagents used in typical runs are also taken from references (24) and (25) and are included to give an idea of the scale of these chemical operations and the yields of product.

[25] S. W. Tobey and R. West, ibid. 88, 2481 (1966).

D. OTHER SPECIES OF INTEREST

Several other compounds are of immediate interest in this research program, but progress on the study of these substances does not warrant more than a passing notation of this time.

1. Cyclopropene

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HC = CH
  \ /
   C
   H2
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This compound is indefinitely stable at 77°K but it slowly polymerizes at dry ice temperature (-78°).[26] We have synthesized this molecule by the reaction of allyl chloride with sodium amide,

$$H_2C = CHCH_2Cl + NaNH_2 \rightarrow$$ 

under conditions where the unstable cyclopropene can readily escape from the reaction mixture and be immediately trapped at 77°K.[27] The apparatus consisted of a three-neck flask heated by a water bath and equipped with a magnetic stirrer. The flask was fitted with an addition funnel, a nitrogen purge-gas inlet capillary, and a jacketed condenser filled with glass helixes and cooled by circulating ice water. The product coming through the column was washed in 2 N sulphuric acid and trapped at 77°K. A pump was connected to this final trap through a drying tube, and in operation the entire system was operated at about 5 in. Hg vacuum. The flask was charged with 12 gm of $NaNH_2$ in 20 ml of mineral oil and was heated to 75°. To this stirred suspension was added dropwise 23 gm of

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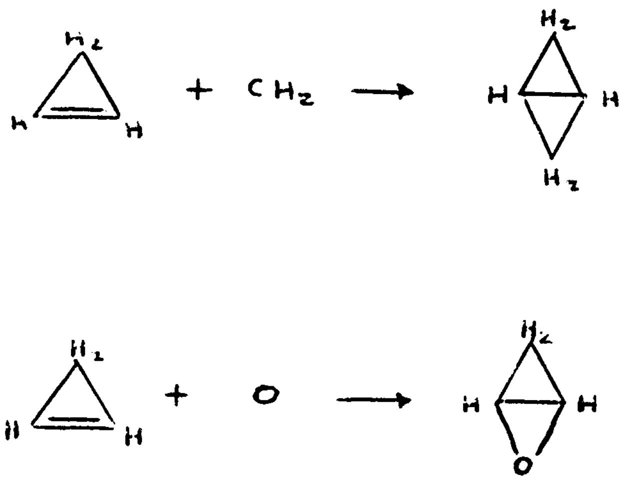
[26] K. B. Wiberg and W. J. Bartley, J. Am. Chem. Soc. 82, 6375 (1960).

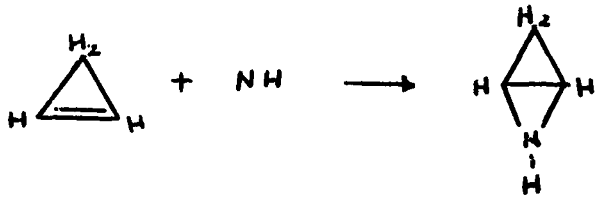
[27] G. L. Closs and K. D. Krantz, J. Org. Chem. 31, 638 (1966).

allyl chloride diluted with 15 ml of mineral oil. The gaseous product was evolved from the reaction mixture, but persistent frothing was a problem. The entrapment of the product in this froth will delay its transport to the 77°K trap to such an extent that the highly reactive product may be lost by polmerization before it ever leaves the reaction flask. The froth was minimized by directing a stream of cold air over the top of the flask not immersed in the hot water bath. The addition of the allyl chloride took 2 to 4 hours and the reaction flask was maintained at 75° for an additional 2 hours while a slow nitrogen gas purge was passed through the entire apparatus. The final product may be purified by simple distillation.

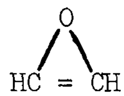
The energetics of cyclopropene are being developed for correlation and comparison with that of cyclopropenone and cyclopropanone.

Addition reactions at low temperatures could lead to interesting products, e.g.,





2. Oxirene



The status of this synthesis is about as described earlier[16] wherein a series of experiments were conducted in which atomic oxygen from a resonant rf discharge was contacted with acetylene in a reactor immersed in liquid oxygen (90°K). This low pressure gas phase reaction was accompanied by a blue-green chemiluminescent flame, yielded a yellow-red solid deposit on the cold walls of the reactor, and underwent both color change and effervescent behavior on warm-up. Only CO_2, $(CHO)_2$, O_2, HCOOH and H_2O were observed during the warm-up of the composite solid product. A point of some note was the absence of ketene in the product mixture, for ketene was formed at 20°K by the reaction of photolytically produced ground state ^3P oxygen atoms (from N_2O) with C_2H_2 in a solid matrix of argon.[28] The failure to observe ketene in our experiment must have been due to the inefficiency of the quenching process. This reaction would be exothermic by 127 kcal/mole.

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[28] I. Haller and G. C. Pimentel, J. Am. Chem. Soc. 84, 2855 (1962).

One would expect oxirene to be formed by the addition of an excited ^1D oxygen atom across the triple bond of acetylene. Recent attempts to identify oxirene from room temperature experiments have failed,[29,30] but with good quenching it should be possible to isolate this very interesting product molecule. Good quenching is even more crucial here than was true for ketene since the ^1D atom is 45 kcal above the ground state ^3P atom. Whereas the earlier experiments involved a quenched low pressure diffusion flame, the more severe quenching requirements have led to an apparatus which permits a mixture of $O(^3P)$ and $O(^1D)$ atoms to be bubbled through either liquid acetylene or through a solution of acetylene in any one of several cryosolvents.

3. Vinyl Alcohol

$$H_2C = CHOH$$

This compound has never been observed, although it is frequently postulated as a reaction intermediate.[31] This molecule apparently undergoes a facile rearrangement to acetaldelyde. We are studying the synthesis of this compound by the reaction of excited atomic oxygen (^1D) with ethylene wherein we expect the oxygen atom to merely insert in the C-H bond. The ground state atom is expected to abstract a hydrogen atom giving the two radicals OH and C_2H_3, both of which would be expected to react further in a complex manner.

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[29] R. N. McDonald and P. A. Schwab, J. Am. Chem. Soc. 86, 4866 (1964).

[30] J. K. Stille and D. S. Whitehurst, J. Am. Chem. Soc. 86, 4871 (1964).

[31] J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", Benjamin, Inc., New York, N. Y., 1965.